JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2024

CHEMISTRY   **9729/02**

Paper 2 Structured Questions   **10 September 2024**
                                                                    2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	7
2	11
3	13
4	14
5	12
6	18
Penalty (delete accordingly)	
Lack **3 sf** in final answer	−1 / NA
Missing/wrong units in final ans	−1 / NA
Bond linkages	−1 / NA
Total	**75**

This document consists of **22** printed pages and **2** blank pages.

Answer **ALL** the questions in the spaces provided.

1   *Use of the Data Booklet is relevant to this question.*

The most recent updates to the Periodic Table occurred in 2016, when IUPAC officially recognised the discovery of four new elements: Nihonium (Nh), Moscovium (Mc), Tennessine (Ts), and Oganesson (Og), completing the seventh row of the table.

Table 1.1 lists the number of protons, neutrons and electrons in four particles, each from one of the elements mentioned above.

Each particle may be an atom, an anion or a cation.

Table 1.1

element	particle	atomic no.	nucleon no.	no. of protons	no. of neutrons	no. of electrons
Nihonium (Nh)	**Nh**	113	286	113	173	113
Moscovium (Mc)	**Mc³⁻**	115	290		175	118
Tennessine (Ts)	**Ts⁻**	117			177	
Oganesson (Og)	**Og**		294	118		118

(a) Based on the positions of the four new elements in the Periodic Table, state the Group that each of the elements belong to.

Nh   ....

Mc   ....

Ts   ....

Og   ....   [1]

(b) Fill in the empty spaces in Table 1.1.   [2]

(c) A stream consisting of α-particles (He^{2+}) is subjected to an electric field as shown in Fig. 1.1 below.
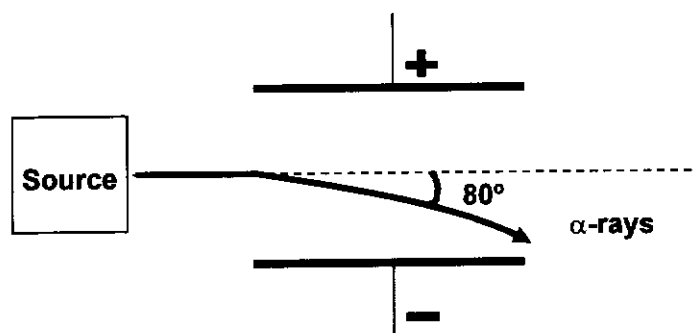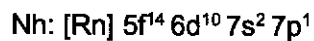

Fig. 1.1

Determine, by calculation, the angle of deflection for a second stream consisting of Mc^{3-} that is passed through the same electric field.

[1]

(d) The simplified electronic configuration of Nihonium is given below.

Nh: $[Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^1$

(i) Using information from Table 1.1, give the simplified electronic configuration of Moscovium (Mc).

....

.... [1]

(ii) Predict if Nh or Mc would have a higher first ionisation energy. Briefly explain your answer.

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.... [2]

[Total: 7]

2 **(a)** Catalytic converters containing platinum solid convert over 90% of carbon monoxide and gaseous nitrogen oxides into harmless gases such as CO_2 and N_2. Outline the mode of action of the platinum catalyst.
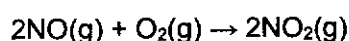
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.... **[2]**

One reaction in which air can be polluted with nitrogen oxides is shown below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

0.05 mol dm^{-3} of NO and 0.005 mol dm^{-3} of O_2 were mixed and the rate of reaction was followed by measuring the concentration of oxygen remaining after various time intervals.
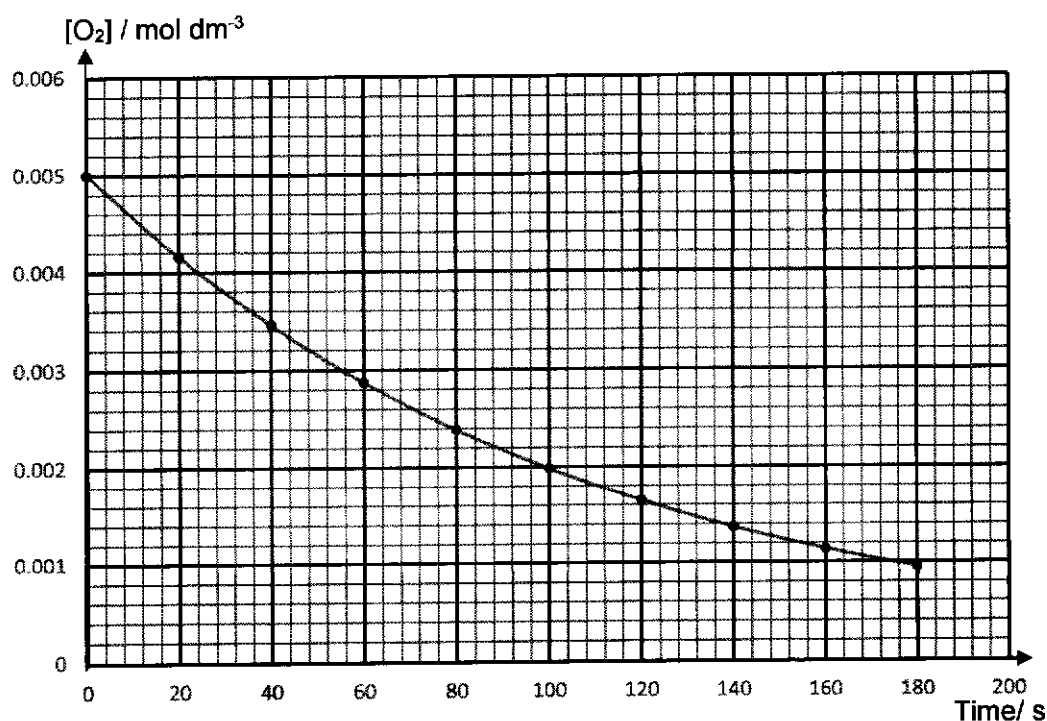
The following graph was obtained in Fig. 2.1.

Fig. 2.1

(b) **(i)** Define the term *half-life* of a reaction.

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.... **[1]**

(ii) Show all your working and draw clearly any construction lines on Fig. 2.1 to determine the order of reaction with respect to O_2.

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.... [2]

(iii) Show all your working and clearly draw any construction lines on Fig. 2.1 to determine the initial rate of reaction. State its units.

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.... [2]

(c) Further experiments were carried out changing the [NO] but keeping the initial $[O_2]$ constant at 0.10 mol dm^{-3}. The following results were obtained.

Table 2.1

Experiment	Initial [NO] / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.01	3.75×10^{-5}
2	0.02	1.50×10^{-4}

(i) Using the data from Table 2.1, deduce the order of reaction with respect to NO.

....

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.... [1]

(ii) Write the rate equation for this reaction.

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.... [1]

(iii) Using Table 2.1, calculate a value for the rate constant. Include units of the rate constant in your answer.
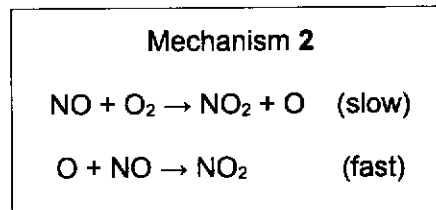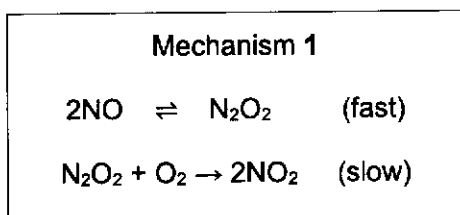
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.... [1]

(d) Two possible mechanisms for this reaction are given below.

State the mechanism which is consistent with the rate equation you have written in **(c)(ii)** and explain your answer.

Mechanism **1**
$2NO \rightleftharpoons N_2O_2$ (fast)
$N_2O_2 + O_2 \rightarrow 2NO_2$ (slow)

Mechanism **2**
$NO + O_2 \rightarrow NO_2 + O$ (slow)
$O + NO \rightarrow NO_2$ (fast)

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.... [1]

[Total: 11]

3 The Wolff-Kishner reaction transforms ketones or aldehydes into alkanes by using hydrazine, N_2H_4 and potassium hydroxide, KOH, as illustrated in equation 1 below.
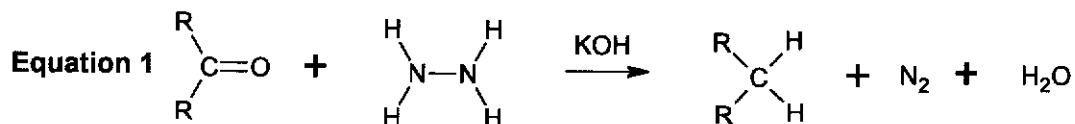
(a) State the type of reaction in equation 1.

.... [1]

(b) Indane, C_9H_{10}, is an ortho-fused bicyclic hydrocarbon consisting of a benzene ring fused to a cyclopentane ring. It is used as an anti-vibration agent for aviation fuel.

Indane can be synthesised from 3-phenylprop-1-ene by the following route, incorporating Wolff-Kishner reaction.
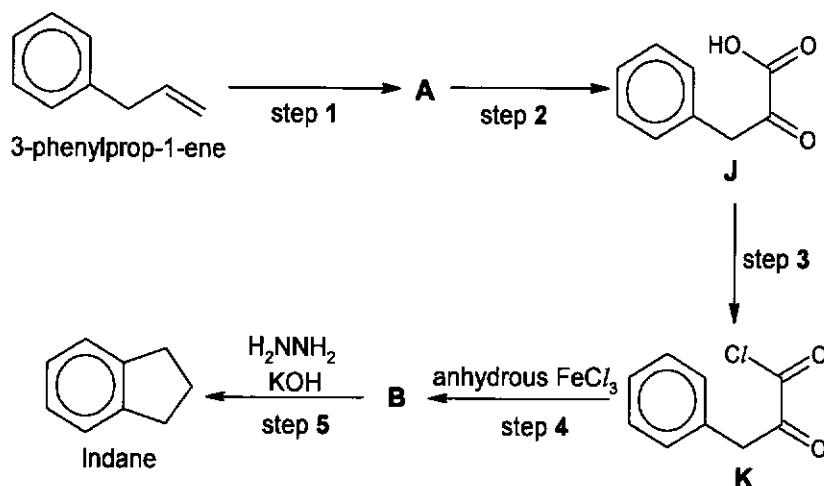
(i) Draw the structures of **A** and **B**.

[2]

(ii) State the reagents and conditions for steps **1**, **2** and **3**.

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.... [3]

(iii) By means of a simple chemical test, distinguish compounds **J** and **K**. State the observations for each compound clearly.
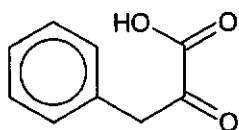
J
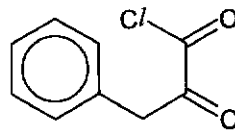
K

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.... [2]

(c) Nitration of 3-phenylprop-1-ene can achieved by reacting it with concentrated H_2SO_4 and concentrated HNO_3.

Name and draw the reaction mechanism for the nitration of 3-phenylprop-1-ene.

[3]

(d) Compound **J** can be used as a starting material to produce a cyclic diester as shown below.
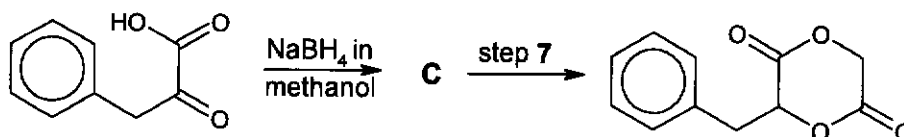
(i) Draw the structure of **C**.

[1]

(ii) Suggest the reagents and conditions for step **7**.

....

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.... [1]

[Total: 13]

4 **(a)** Compound **D** is a sweet-smelling organic compound with the molecular formula $C_5H_9BrO_2$. It is known that each molecule of **D** contains two functional groups.

A student from JPJC was tasked to determine the structure of compound **D**.

Table 4.1 below shows the chemical reactions that the student carried out for compound **D**.

Table 4.1

expt	reagent	Result
1	$AgNO_3(aq)$, warm	cream precipitate formed which was soluble in an excess of $NH_3(aq)$.
2	$NaOH(aq)$, heat	two products were formed; **E** ($C_3H_5O_3Na$) and **F** (C_2H_6O).

(i) State the identity of the cream precipitate formed in experiment 1.

Hence or otherwise, name the functional group, shown by experiment 1, that is present in compound **D**.

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.... [1]

(ii) State the type of reaction undergone in reaction 2 and identify the other functional group in **D**.

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.... [1]

The student conducted further chemical tests on compounds **E** and **F** separately. The results of the tests are given in Table 4.2.

Table 4.2

experiment	reagent	Result
3	$PCl_5(s)$	misty fumes were formed for both **E** and **F**.
4	I_2, $NaOH(aq)$, warm	pale yellow precipitate formed for both **E** and **F**.

(iii) Based on both experiments **3** and **4**, what is the common functional group that could be present in both compounds **E** and **F**? Explain your answer, giving the type of reaction undergone.

....

.... [1]

(iv) Using your answers in **(a)(i)**, **(a)(ii) and (a)(iii)**, draw the structures of compounds **E** and **F**.

[2]

(v) The student now has enough information to determine the structural formula of **D**.

Draw the fully displayed structure of **D**.

[1]

(b) Dichlorodiphenyltrichloroethane (DDT) is an organochlorine pesticide that was widely used during the 20th century for controlling insect-borne diseases like malaria.

The equation below shows the environmental degradation of DDT to dichlorodiphenyldichloroethylene (DDE).

DDT   DDE
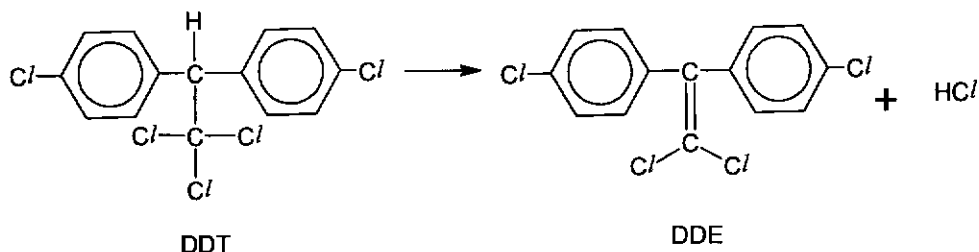
(i) State the type of reaction for the conversion of DDT to DDE.

....

.... [1]

Table 4.3 below shows the results when aqueous silver nitrate is heated with 0.5 mol of DDT and 0.5 mol of DDE separately.

Table 4.3

	Time taken for precipitate (ppt) to appear	No. of moles of ppt formed per mole of compound reacted
DDT	5 min	x mol
DDE	no ppt	0 mol

(ii) State the value of x in Table 4.3.

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.... [1]

(iii) Explain why no precipitate was observed for the reaction with DDE.

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.... [2]

(iv) In organic chemistry, a geminal compound is a molecule in which 2 or more identical or similar functional groups are attached to the same carbon atom.

When DDT reacts with hot aqueous NaOH, a gem-triol, is formed as an intermediate. A gem-triol contains three -OH groups bonded to the same carbon atom. The gem-triol formed is unstable and it readily converts to the final product, **S**.

S reacts with aqueous $Na_2CO_3(aq)$ to liberate a colourless gas.

Draw the structure of the organic compound **S**.

[1]

(c) **(i)** 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane, or o,p'-DDT, is an constitutional isomer of DDT. The structure of o,p'-DDT is given below.
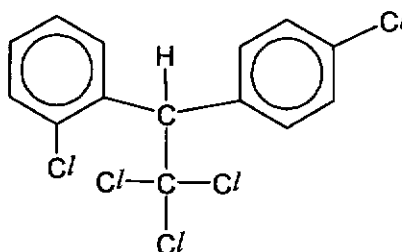
o,p'-DDT

State the type of stereoisomerism exhibited by o,p'-DDT.

....

.... [1]

(ii) Draw the stereoisomers of o,p'-DDT.

[2]

[Total: 14]

5 The pH of the seawater in the ocean is regulated by the carbonate - bicarbonate (CO_3^{2-} / HCO_3^-) buffer system.

Main buffering system:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$
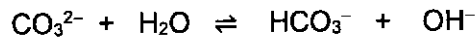
Recently, changes in the pH of the oceans by ocean acidification has been a concern. Ocean acidification, primarily caused by the absorption of carbon dioxide, CO_2, from the atmosphere, poses a significant threat to marine ecosystems worldwide.

The increased concentration of CO_2 in seawater leads to changes in the pH as shown in Fig. 5.1 below which shows the average ocean pH level worldwide from 1985 to 2020.
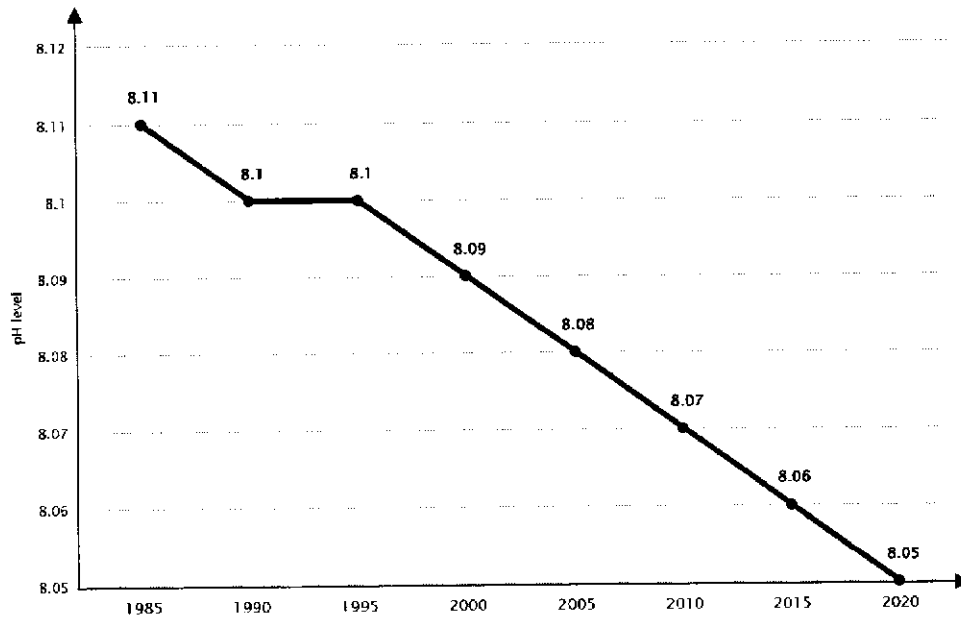
Fig. 5.1

(a) **(i)** Using Fig. 5.1, state and explain the trend of the pH of the seawater of the ocean.

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.... **[1]**

(ii) With the aid of equations show how the carbonate - bicarbonate buffer system in seawater maintains the pH when there is an increase in amounts of H^+ or OH^- in the seawater.

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.... **[2]**

(iii) Use the pH value from Fig. 5.1, show that the molar ratio of bicarbonate to carbonate ion of a sample of seawater from 2020 is 89:1.

Given that the K_b of CO_3^{2-} is 1.0×10^{-4} mol dm^{-3}.

[2]

The total CO_3^{2-} + HCO_3^- content of the seawater can be found by boiling a seawater sample with an excess of dilute sulfuric acid and absorbing the CO_2 evolved in a solution of barium hydroxide, $Ba(OH)_2$.

The precipitated barium carbonate, $BaCO_3$ can be filtered off, dried and weighed.

When a 100 cm^3 seawater sample was treated in the above-mentioned process, 0.281 g of $BaCO_3$ was produced.

[Assume that the seawater sample is from the year 2020]

(iv) Show that the total amount of CO_3^{2-} + HCO_3^- content in the seawater sample is 1.42×10^{-3} mol.

[1]

(v) Hence, using the information in (a)(iii) & (a)(iv) calculate $[CO_3^{2-}]$ in the 100 cm^3 seawater sample from 2020.

[2]

(b) Organisms with calcium carbonate shells produce their shells according to the equation shown.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$
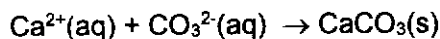
Changes in the pH alters the chemical balance of the oceans and affects marine life, particularly organisms with calcium carbonate shells.

(i) Using the equations below and the concept of Le Chatelier's principle and solubility product, explain why marine organisms will not be able to build shells if pH of the seawater decreases.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s) \text{ -----(1)}$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \text{ -----(2)}$$

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.... [2]
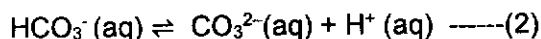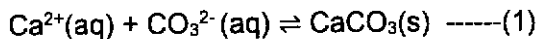
(ii) The concentration of Ca^{2+} ions in the seawater sample from 2020 is 3.99×10^{-4} mol dm^{-3}.

Given that K_{sp} CaCO$_3$ is 3.30×10^{-9} mol^2 dm^{-6}, calculate the minimum $[CO_3^{2-}]$ for the organisms to form their shells in 2020.

[1]

(iii) Using your answer in **(a)(v)** and **(b)(ii)**, explain whether the organisms will be able to form their shells in the seawater in 2020?

[1]

[Total: 12]

6 **(a)** Haemoglobin and hemocyanin are two oxygen-transporting proteins found in living organisms. Both proteins are coloured due to the presence of transition metals, such as iron in haemoglobin and copper in hemocyanin, that form complexes essential for their oxygen-binding properties.

    (i) Why are transition metal complexes coloured?

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.... [3]

    (ii) Non-transition metal compounds, in contrast, tend to be colourless.

Explain why a solution containing $[Mg(H_2O)_6]^{2+}$ is colourless.

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.... [1]

Absorption spectra, an analytical method in chemistry, show the wavelengths of light absorbed by substances.

Chemists use this technique to analyse the oxygenated blood samples from sheep (haemoglobin) and spiders (haemocyanin) to compare their absorption characteristics.
The result of the analysis is shown in Fig. 6.1.

Relative absorbance
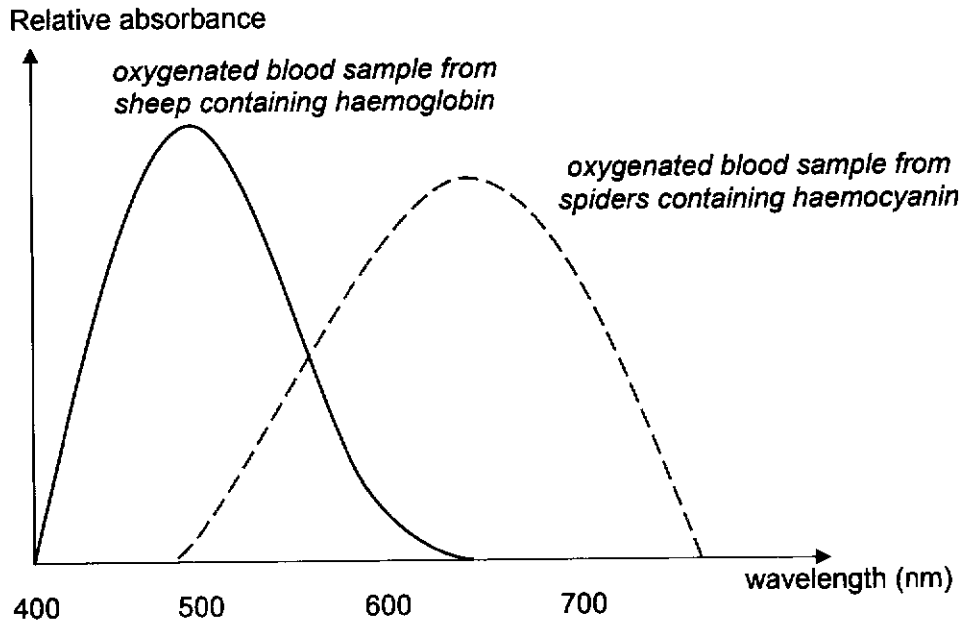
Fig. 6.1: Graph showing Absorption Spectra

The wavelengths associated with each colour of visible light are given below in Table 6.1. Light of a longer wavelength is lower in energy than light of a shorter wavelength.

Table 6.1

colour of visible light	wavelength (nm)
Red	620 – 750
Orange	590 – 620
Yellow	570 – 590
Green	495 – 570
Blue	450 – 495
Violet	380 – 450

(iii)   The oxygenated blood of sheep, which contains haemoglobin, is red.

Using this information and the data provided, predict the colour of the oxygenated blood of spiders, which contains haemocyanin.

....

....   [1]

(iv) What deduction can be made from the absorption spectra in Fig. 6.1, about the size of the d-orbital splitting in the two samples of oxygenated blood, containing different complexes of haemoglobin and haemocyanin?

Explain your answer.

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.... [2]

(b) The van Arkel triangle, invented by Dutch chemist Anton Eduard van Arkel, is a tool used to classify the bonding in compounds as ionic, covalent, or metallic.

Fig. 6.2 shows an example of a van Arkel triangle.

The y-axis represents the difference in electronegativity between two elements, while the x-axis shows the average electronegativity of the two elements.

increasing average electronegativity
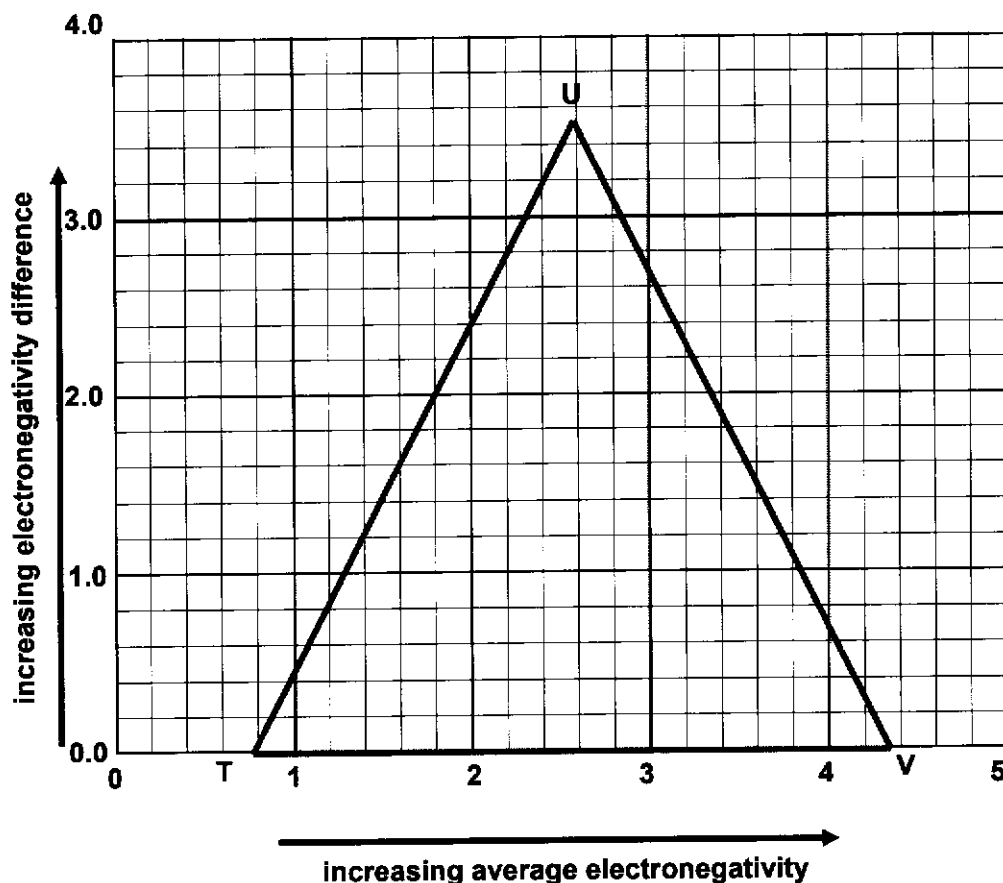
Fig. 6.2

Table 6.2 provides the electronegativity values of some of elements from Period 3 of the Periodic Table, based on Pauling's Scale. The average electronegativity is calculated based on the sum of the electronegativities of the two elements in the compound, divided by two.

Table 6.2

Element	Electronegativity
Na	0.9
Mg	1.2
A*l*	1.5
Si	1.8
P	2.1
S	2.5
C*l*	3.0

(i) Plot the position of Cl_2 and $AlCl_3$ on the diagram. Label your points clearly in Fig. 6.2.

[2]

(ii) The three extremes on the van Arkel triangle, namely **T**, **U** and **V**, represent the three types of chemical bonding, metallic, ionic and covalent.

State the correct type of bonding present at each of the bonding extremes.

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.... [2]

(c) (i) In the liquid state, $AlCl_3$ exists as a compound with a molar mass of 267 g mol^{-1}.

Draw the structure of this compound.

[1]

(ii) The boiling points of Al_2O_3 and $AlCl_3$ in the liquid state are 2977 °C and 180 °C respectively.

Explain, in terms of structure and bonding, the difference in their boiling points.

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.... [2]

(iii) The pH values of the solutions of two Period 3 chlorides are given below in Table 6.3.

Table 6.3

compound	pH of 1.0 mol dm^{-3} solution
MgCl_2	**X**
AlCl_3	**Y**

Write equations for the reaction of AlCl_3 with water.

State the values of x and y in Table 6.3 above. Briefly explain the different pH values of the two chloride solutions.

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.... **[3]**

(iv) The lattice energy of magnesium chloride is -2582 kJ mol^{-1}. Some enthalpy changes of hydration are listed in Table 6.4.

Table 6.4

Ions	ΔH_{hyd} / kJ mol^{-1}
Mg^{2+}	-1980
Cl^-	-381

Using the data provided, calculate the enthalpy change of solution of magnesium chloride.

[1]

[Total: 18]

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𝒿𝑃 **JURONG PIONEER JUNIOR COLLEGE**
JC2 PRELIMINARY EXAMINATION 2024

CHEMISTRY

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9729/02

10 September 2024
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Candidates answer on the Question Paper.

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Total	**75**

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This document consists of **19** printed pages and **1** blank page.

[Turn Over

1   *Use of the Data Booklet is relevant to this question.*

The most recent updates to the Periodic Table occurred in 2016, when IUPAC officially recognised the discovery of four new elements: Nihonium (Nh), Moscovium (Mc), Tennessine (Ts), and Oganesson (Og), completing the seventh row of the table.

Table 1.1 lists the number of protons, neutrons and electrons in four particles, each from one of the elements mentioned above. Each particle may be an atom, an anion or a cation.

Table 1.1

element	particle	atomic no.	nucleon no.	no. of protons	no. of neutrons	no. of electrons
Nihonium (Nh)	**Nh**	113	286	113	173	113
Moscovium (Mc)	**Mc^{3-}**	115	290		175	118
Tennessine (Ts)	**Ts$^-$**	117			177	
Oganesson (Og)	**Og**		294	118		118

(a)   Based on the positions of the four new elements in the Periodic Table, state the Group that each of the elements belong to.

Nh   ....

Mc   ....

Ts   ....

Og   ....

Nh: Group 13

Mc: Group 15

Ts: Group 17

Og: Group 18

All groups correct. Do not accept Group 3, 5, 7, 0. **[1]**

[1]

Examiner's comments:

Students would need to recall that elements in the periodic table are arranged according to their <u>atomic number / proton number</u>.

By referring to the Data Booklet, it is clear that the 4 missing elements belong to Group 13, 15, 17 and 18 respectively.

▓▓	14	▓▓	16	▓▓	▓▓
					2 He helium 4.0
5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium ~	85 At astatine ~	86 Rn radon ~
✓	114 Fl flerovium ~	✓	116 Lv livermorium ~	✓	✓

Common mistakes that are not accepted:

- Group 3, 5, 7, 8, 0
- Group III, V, VII, VIII, VIII

(b) Fill in the empty spaces in Table 1.1.

element	parti-cle	atomic no.	nucleon no.	no. of protons	no. of neutrons	no. of electrons
Nihonium (Nh)	**Nh**	113	286	113	173	113
Moscovium (Mc)	**Mc^{3-}**	115	290	**115**	175	118
Tennessine (Ts)	**Ts$^-$**	117	**294**	**117**	177	**118**
Oganesson (Og)	**Og**	**118**	294	118	**176**	118

[2]

Examiner's comments:

Generally, quite well done. A few careless mistakes.

Students need to understand the following:

- Atomic no. = no. of protons
- Nucleon no. = no. of protons + no. of neutrons
- To find no. of electrons:
  - For cations: take away the relevant no. of electrons
  - For anions: add the relevant no. of electrons

(c) A stream consisting of α-particles (He^{2+}) is subjected to an electric field as shown in Fig. 1.1 below.

Fig. 1.1
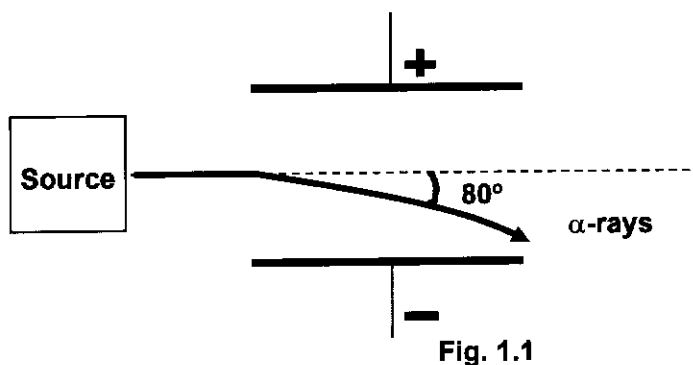
Determine, by calculation, the angle of deflection for a second stream consisting of Mc^{3-} that is passed through the same electric field.

Since **angle of deflection α charge/mass,**

$$\frac{\text{angle of deflection of } \alpha\text{-particles}}{\text{angle of deflection of } Mc^{3-}} = \frac{2/4}{3/290}$$

[1]

Solving, angle of deflection of Mc^{3-} = -1.6551 ≈ **-1.66°**

Examiner's comments:
Not so well done.

Key concept here is that the **angle of deflection α charge/mass**.

Common mistakes:
- did not apply the correct formula;
- did not indicate – or state towards the positive plate to show direction (did not penalise this time round);
- did not round off to 3 s.f.

(d) The simplified electronic configuration of Nihonium is given below.
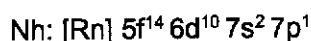
Nh: [Rn] $5f^{14}\,6d^{10}\,7s^2\,7p^1$

(i) Using information from Table 1.1, give the simplified electronic configuration of Moscovium (Mc).

Mc: [Rn] $5f^{14}\,6d^{10}\,7s^2\,7p^3$

[1]
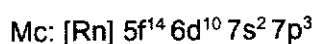
Examiner's comments:
This was meant to be quite a doable part of the question but there were quite a number of mistakes. Looking at the atomic/proton numbers, Mc should have 2 more electrons than Nh.

Common mistakes that are not given credit:
- $5f^{14}\,6d^{10}\,7s^2\,7p^3$
- [Rn] $5f^{14}\,6d^{10}\,7s^2\,7p^6$

(ii) Predict if Nh or Mc would have a higher first ionisation energy. Briefly explain your answer.

Mc would have a <u>higher first ionisation energy</u> than Nh.

Across the period, <u>nuclear charge increases</u> while <u>shielding effect remains constant</u>, leading to an <u>increase in effective nuclear charge</u> OR <u>strong nuclear attractions on the valence electrons</u>

[2]

<u>Examiner's comments:</u>
This part was generally well done.

A common mistake was to use the explanation of increasing IE down a group, i.e. increase in shielding effect outweighs increase in nuclear charge, rather than across a period.

Another point that students tend to miss out is the increase in nuclear charge which is due to an increase in proton number. Please take note that nuclear charge is NOT equivalent to effective nuclear charge.

[Total: 7]

2 (a) Catalytic converters containing platinum solid convert over 90% of carbon monoxide and gaseous nitrogen oxides into harmless gases such as CO_2 and N_2.

Outline the mode of action of the platinum catalyst.

The catalyst in the catalytic converter is a <u>heterogeneous</u> catalyst.

The reactant molecules **adsorb**(*) onto the surface of the metal catalyst (Pd & Pt) via **formation** of **weak (temporary) bonds**.

This **weakens the bonds in the reactant molecules** and thus provides an alternative reaction mechanism of **lower activation energy**. The <u>surface concentration of the reactants also increases.</u>

The **product molecules desorbs from the catalyst surface, making the surface available for adsorption of new reactant molecules**.

[2]

<u>Examiner's comments:</u>
This part was not so well done.

Students need to understand and apply the mode of action for heterogenous catalyst. Some wrote as homogenous/heterozygous/heterolytic etc, which were all incorrect.

The key mode of actions would include:
- Adsorption (not absorption)
- Reaction (weaking of bonds and forming of new bonds)
- Desorption

One reaction in which air can be polluted with nitrogen oxides is shown below.
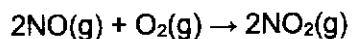
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

0.05 mol dm^{-3} of NO and 0.005 mol dm^{-3} of O_2 were mixed and the rate of reaction was followed by measuring the concentration of oxygen remaining after various time intervals.

The following graph was obtained.

Graph **2.1**
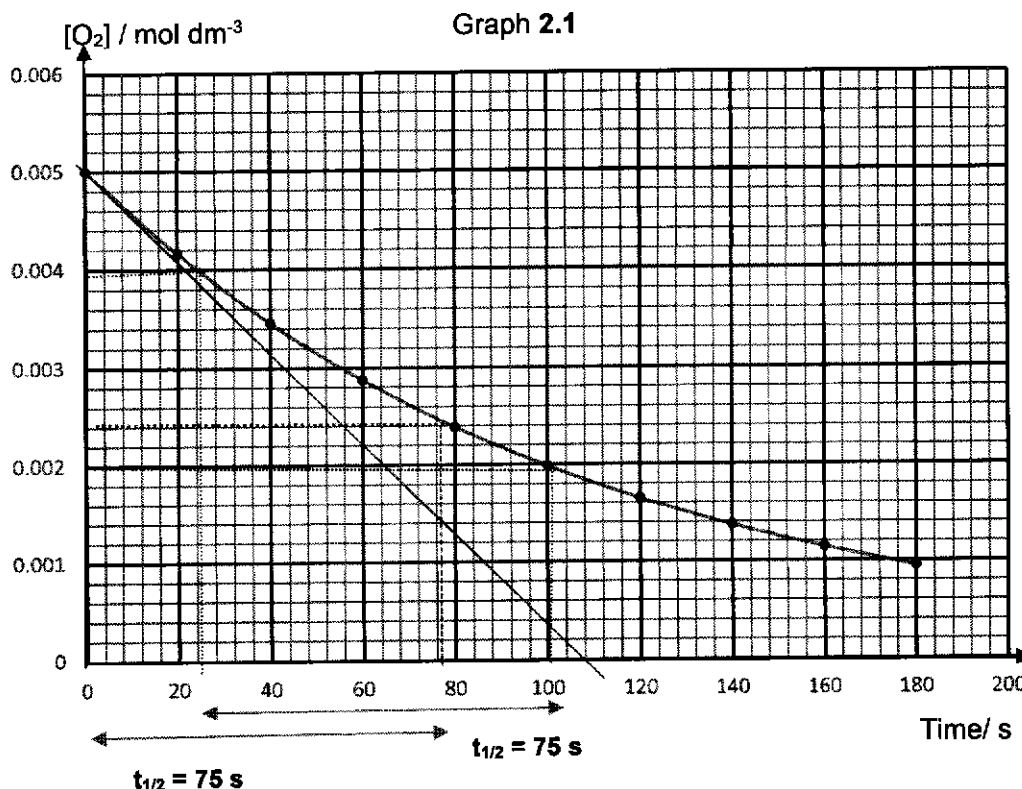
(b) **(i)** Define the term *half-life* of a reaction.

Half-life, $t_{1/2}$, is the <u>time taken</u> for the <u>reactant concentration to decrease to half of its original/ initial value</u>. [1]

Examiner's comments:
This part was well done.

But there were a few mistakes made by candidates:
- "product concentration" or not stating that it refers to reactant concentration/amount.
- concentration of <u>reactant**s**</u>: Please take note that half-life is in reference to only 1 reactant. (did not penalise)
- "decrease by 2".

(ii) Show all your working and draw clearly any construction lines on the Graph 2.1 to determine the order of reaction with respect to O_2.

($\checkmark$) construction lines for two $t_{1/2}$ + labelled as $t_{1/2}$ or values on graph
($\checkmark$) two correctly read $t_{1/2}$ values either stated or indicated on graph

Using graph of [NO] = 0.10 mol dm^{-3},

When concentration of [O_2] decreases from 0.0050 mol dm^{-3} to 0.0025 mol dm^{-3}, half life = <u>75 s</u>

When [O_2] decreases from 0.0040 mol dm^{-3} to 0.0020 mol dm^{-3} (halved), half-life = <u>75 s</u> (can be average or either half-life)

Since <u>half-lives are constant</u> ($\checkmark$), the order of reaction with respect to O_2 is <u>1</u>. ($\checkmark$)

[2]

<u>Examiner's comments</u>:
This part was generally well done.

A few things to take note:
- do indicate clearly on the graph **where are the half-lives** and **the values** for the examiners;
- it is important to use "consecutive half-lives". (not penalised this time round);
- some students read off the graphs wrongly for half-life.
  Eg. 0.005 to 0.002; 0.0025 to 0.001 [incorrect examples]

(iii) Show all your working and clearly draw any construction lines on the Graph 2.1 to determine the initial rate of reaction. Include its units.

Initial Rate Method – draw a gradient at t = 0 min

Gradient = (0.005 - 0) / (0 - 108) = - 4.63 x 10^{-5} mol dm^{-3} s^{-1}

Take modulus and ignore the negative sign;

hence rate is 4.63 x 10^{-5} mol dm^{-3} s^{-1}

[2]

<u>Examiner's comments</u>:
The part was generally well done.

The few things to take note:
- rate is ALWAYS positive. No such thing as a negative rate of reaction.
  As such, initial rate = | gradient |
- Quite a handful of students did not know how to construct the tangent to the curve at t = 0s properly. Consequently, the value of their rate is either too high or too low.
  The range that was accepted was ±20%.
  3.70 x 10^{-5} to 5.56 x 10^{-5}
  Students are strongly encouraged to purchase a curved ruler and learn how to use it to draw a tangent to the curve at any point.

(c) Further experiments were carried out changing the [NO] but keeping the initial [O_2] constant at 0.10 mol dm^{-3}. The following results were obtained.

Table 2.1

Experiment	Initial [NO] / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.01	3.75 x 10^{-5}
2	0.02	1.50 x 10^{-4}

(i) Using the data from the Table 2.1, deduce the order of reaction with respect to NO.

Let **rate** $\propto$ **[NO]^a**.

$$\frac{(rate)_2}{(rate)_1} = \frac{1.50 \times 10^{-4}}{3.75 \times 10^{-5}} = \frac{(0.02)^b}{(0.01)^b}$$

$$4 = 2^b \qquad \therefore b = 2$$

OR, When **[NO] is x2 or doubled** while keeping [O_2] constant, **initial rate is x4 or quadrupled**.

$\therefore$ the order of reaction with respect to [NO] is **2**.   [1]

Examiner's comments:

* This was well answered.
* Students should avoid using "increases" or "decreases" as some incorrectly stated that "the initial rate is decreased/reduced to 4x" instead of "to ¼ x".

(ii) Write the rate equation for this reaction.

rate = k[NO]^2[O_2]   [1]

Examiner's comments:

* This was well answered.
* Some forgot to include [O_2].

(iii) Using **Table 2.1**, calculate a value for the rate constant. Include units of rate constant in your answer.

$$3.75 \times 10^{-5} = k\,(0.01)^2\,(0.1)$$

OR, $\quad 1.50 \times 10^{-4} = k\,(0.02)^2\,(0.1)$

$\underline{k = 3.75 \text{ mol}^{-2} \text{ dm}^6 \text{ min}^{-1}}$ **[1] ecf + correct value + units** [1]

Examiner's comments:

* Many could not derive the correct units for k.
* Many stated 's^{-1}' instead of 'min^{-1}'.
* Some did not use the data in **Table 2.1**.

(d) Two possible mechanisms for this reaction are given below.

Mechanism **1**
$2NO \rightleftharpoons N_2O_2$ (fast)
$N_2O_2 + O_2 \rightarrow 2NO_2$ (slow)

Mechanism **1**
$NO + O_2 \rightarrow NO_2 + O$ (slow)
$O + NO \rightarrow NO_2$ (fast)

State the mechanism which is consistent with the rate equation you have written in **(c)(ii)** and explain your answer.

Mechanism 1 (✓)

From step 1, $K_c = \dfrac{[N_2O_2]}{[NO]^2}$ or $k_f[NO]^2 = k_b[N_2O_2]$

$[N_2O_2] = K_c [NO]^2$ $[N_2O_2] = \dfrac{k_f}{k_b} [NO]^2$

From the slow step which is the **rate-determining step**,

rate = k' [N$_2$O$_2$] [O$_2$] (✓)

$= k' K_c [NO]^2 [O_2]$ (or $k' \dfrac{k_f}{k_b} [NO]^2 [O_2]$)

$\Rightarrow$ **rate = k [NO]^2[O$_2$]**, (✓) where $k = k'K_c$ (or $k = k' \dfrac{k_f}{k_b}$) = constant.

OR,

Since the **rate-determining step** (slow step) **involves one N$_2$O$_2$ molecule and one O$_2$ molecule** (✓) colliding together, **rate $\propto$ [N$_2$O$_2$][O$_2$]**.

Since N_2O_2 is the intermediate and **one N$_2$O$_2$ molecule is formed from two NO molecules** (✓) in step 1 *i.e.* [N$_2$O$_2$] $\propto$ [NO]^2, the **overall rate $\propto$ [NO]^2[O$_2$]**.   [1]

Examiner's comments:

• A small proportion of students could explain their choice of mechanism at molecular level with reference to the slow step.

• Common mistakes were to state "one mole" of reactant colliding with "one mole" of another reactant or did not state the number of particles involved in the rate-determining step.

[Total: 11]

3 The Wolff-Kishner reaction transforms ketones or aldehydes into alkanes by using hydrazine, N_2H_4 and potassium hydroxide, KOH. An example of such a reaction is shown in equation 1 below.

Equation 1
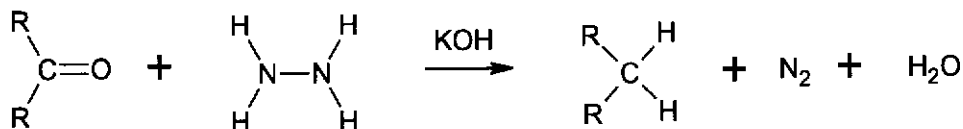
(a) State the type of reaction in equation 1.

When ketone/aldehyde is transformed to alkane, an O atom is lost and two H atoms are gained.

Reduction   [1]

Examiner's comments:

• Only a small proportion of students stated the type of reaction correctly.

• Students should name the reaction w.r.t to the organic reagent undergoing the reaction. For example, when an aldehyde is oxidised to a carboxylic acid with acidified $KMnO_4$, we name this reaction "oxidation" rather than "redox".

• Common responses are "redox", "nucleophilic addition" & "condensation".

(b) Indane, C_9H_{10}, is an ortho-fused bicyclic hydrocarbon consisting of a benzene ring fused to a cyclopentane ring. It is used as an anti-vibration agent for aviation fuel.

Indane can be synthesised from 3-phenylprop-1-ene by the following route, incorporating Wolff-Kishner reaction.
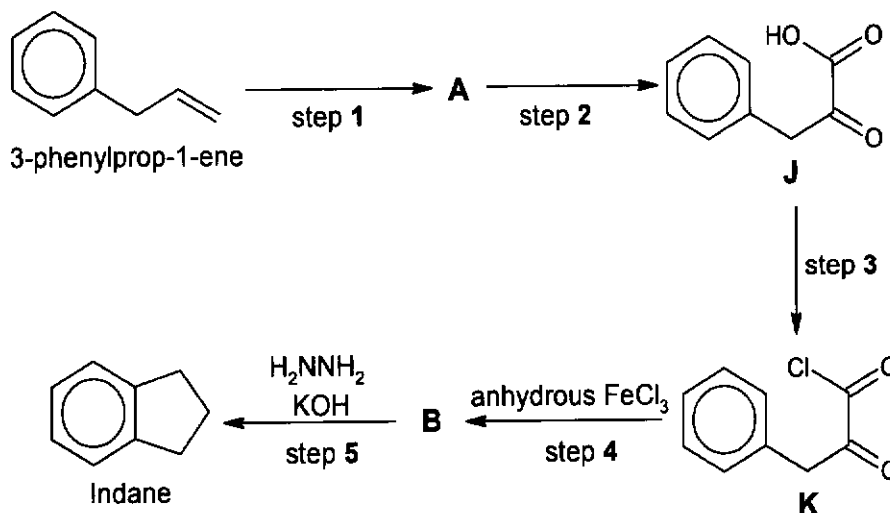
(i) Draw the structures of **A** and **B**.

| **A** | **B** | [2] |
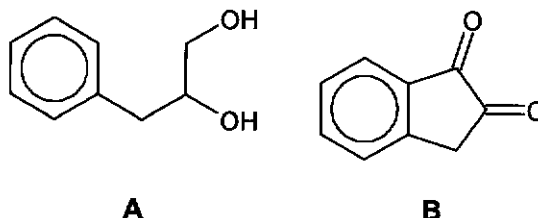
Examiner's comments:

- This was generally not well answered.
- More students could give structure **A** correctly than **B**.

(ii) State the reagents and conditions for steps **1**, **2** and **3**.

> step 1: <u>**cold, KMnO₄(aq), NaOH(aq)**</u> (or <u>**H₂SO₄(aq)**</u>)
> **must state "aqueous" or "dilute".**

> step 2: <u>**K₂Cr₂O₇(aq), H₂SO₄(aq), heat under reflux**</u>
> **must state "aqueous" once.**

> step 3: <u>**PCl₅**</u>, r.t. or <u>**PCl₃, heat**</u> or <u>**SOCl₂, heat**</u>
> **reject "aq". BOD for "PCl₅, heat"**

[3]

Examiner's comments:

- For **step 1**: this was generally not well answered.
  "<u>cold and aqueous/dilute</u> KMnO₄" must be stated to earn the credit.
- For **step 2**: Only a small proportion of students gave the correct answer.
  Common mistakes were stating "KMnO₄", "heat" without reflux or "heat with immediate distillation".
  Students should recognise that benzylic H atoms are present in **A** and that it would be converted to benzoic acid if "KMnO₄(aq) in H₂SO₄(aq), heat" was used.
- For **step 3**: students often gave the correct answer.
  BOD was given for "PCl₅, heat" or "PCl₅(g)/PCl₃(g)/SOCl₂(g)".
  Students should know the physical states of these reagents: PCl₅(s), PCl₃(l) & SOCl₂(l)". As such, students are advised <u>not to give state symbol</u>.
  As PCl₅, PCl₃ and SOCl₂ can undergo hydrolysis readily in the presence of water, these reagents must be <u>dry/anhydrous</u>. Hence, those who stated "aq" were marked down.

(iii) By means of a simple chemical test, distinguish compounds **J** and **K**.
Identify the difference in functional group:

Carboxylic acid   acyl chloride

J   **K**
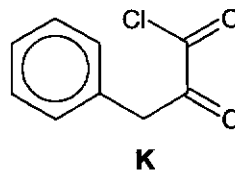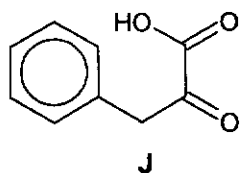
Reagent & conditions: **aqueous AgNO₃ reject with heating (acyl chloride is very reactive and does not need heat, rtp suffices)**

Observations: **White ppt.** of AgC*l* will be seen **immediately for K**.

No white ppt. will be formed **for J**.

OR

Reagent & conditions: **PC*l*₅** or **heat with SOC*l*₂**

Observations: **White fumes** of HC*l* will be seen **for J**.

No white fumes will be seen **for K**.

OR

Reagent & conditions: **Na(s)** or **Mg(s)**

Observations: **For J, effervescence** is seen and H₂ **gas evolved pops with a lighted splint.**

No effervescence of H₂ gas will be seen **for K**.

OR

Reagent & conditions: **A few drops of water** *(given in 2019 P2 Q4(a))* **[1]**

Observations: **For K, gas** of HC*l* which **turns damp blue litmus paper red** will be formed.

No gas of HC*l* will be formed **for J**.

[2]

Examiner's comments:

- A significant number of students used "Na₂CO₃(aq)/NaHCO₃(aq)" test which was rejected.

  Students must know that without water, RCOOH would not give H⁺ to undergo acid-base reaction with Na₂CO₃(s)/NaHCO₃(s). Hence, to test for RCOOH, the reagent must be Na₂CO₃(aq) or NaHCO₃(aq).

  With the presence of water from the aqueous reagent, acyl chloride K would undergo hydrolysis readily to give a carboxylic acid and a strong HC*l*(aq) acid. Hence both J and K would undergo acid-base reaction in this test to give effervescence of CO₂.

- Some students used "water" and stated that K would give white fumes of HC*l*. This test was rejected as with (excess) water, HC*l*(aq) would be formed readily and white fumes might not be seen. However, credit was given to students who stated "add a few drops of water" but "white fumes" would not earn the credit for observation.

(c) Nitration of 3-phenylprop-1-ene can achieved by reacting it with conc H_2SO_4 and conc HNO_3.

Name and draw the reaction mechanism for the nitration of 3-phenylprop-1-ene.

<u>Electrophilic substitution</u> correct spelling

<u>HNO_3 + H_2SO_4 → NO_2^+ + HSO_4^- + H_2O</u>
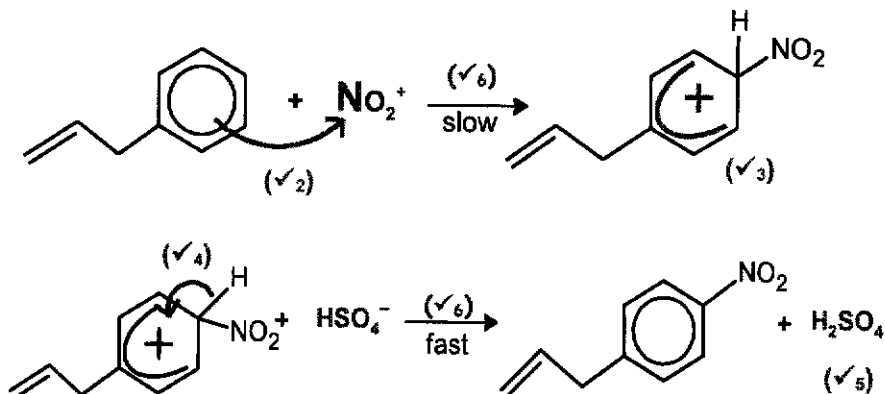
($\checkmark_1$) - balanced equation for the **<u>generation of NO_2^+</u>** electrophile.

($\checkmark_2$) - **<u>full arrow from</u>** π electron cloud of **<u>benzene ring to N</u>** of NO_2^+.

($\checkmark_3$) - **<u>arenium ion with delocalisation of +ve charge over 5 sp^2 C</u>** (not at the sp^3 C) and **<u>NO_2^+ directed to 2- or 4-position</u>** w.r.t. the alkyl side chain.

($\checkmark_4$) - **<u>full arrow from C–H bond</u>** (not from H) **<u>to the +ve charge</u>** of arenium ion

($\checkmark_5$) - **<u>correct product with regeneration of H_2SO_4</u>** catalyst & **<u>balanced eqn</u>**.

($\checkmark_6$) - correctly labelled the **<u>"slow" and "fast" steps</u>** [3]

Examiner's comments:

- This was generally well answered.
- Some students forgot to name the mechanism.
- Some students gave product with —NO_2 substituted at 3-position w.r.t. the side-chain. Students should recognise that the C of the hydrocarbon side-chain directly bonded to the benzene ring is sp^3 <u>hybridised</u> and so this side-chain is considered as <u>an alkyl group</u> which is ring-activating and <u>2,4-directing</u>.
- Students should be more precise in drawing the two curly arrows and the delocalised curve of +ve charge (the +ve charge should be placed 'inside' the delocalised curve and <u>not at the sp^3 carbon</u> with —NO_2). As such, students are advised to <u>draw bigger arenium ion</u>.

(d) Compound **J** can be used as a starting material to produce a cyclic diester as shown below.
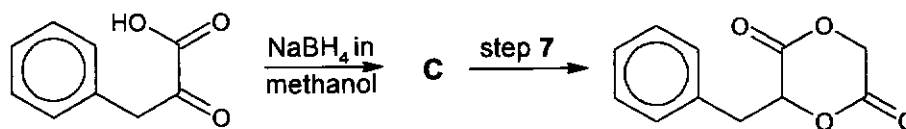
(i) Draw the structure of **C**.

[1]
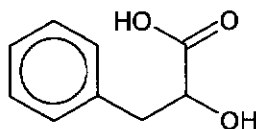
Examiner's comments:
- This was generally not well answered.

(ii) Suggest the reagent and conditions for step **7**.

HOCH₂COOH, concentrated H₂SO₄, heat [1]

Examiner's comments:
- This proved difficult for many students.
- For those who could figure out the organic reagent tend to get the conditions wrong. They omitted "heat" or used "H₂SO₄(aq)".
- BOD was given to "conc. H₂SO₄(aq)" although "aq" was a wrong state symbol for concentrated H₂SO₄. Students are advised not to give state symbol for conc. H₂SO₄. Just state "concentrated H₂SO₄".

[Total: 14]

4   (a)   Compound **D** is a sweet-smelling organic compound with the molecular formula $C_5H_9BrO_2$. It is known that each molecule of **D** contains two functional groups.

A student from JPJC was tasked to determine the structure of compound **D**.

Table 4.1 below shows the chemical reactions that the student carried out for compound **D**.

Table 4.1

expt	reagent	Result
1	AgNO$_3$(aq), warm	cream precipitate formed which was soluble in an excess of NH$_3$(aq).
2	NaOH(aq), heat	two products were formed; compound **E** (C$_3$H$_5$O$_3$Na) and compound **F** (C$_2$H$_6$O).

(i)   State the identity of the cream precipitate formed in experiment 1.

Hence or otherwise, name the functional group, shown by experiment 1, that is present in compound **D**.

silver bromide/ AgBr (✓)
alkyl bromide / bromoalkane / halogenoalkane (✓)   [1]

Examiner's comments:
*   This was generally well answered.

(ii)   State the type of reaction undergone in reaction 2 and identify the other functional group in D.
Alkaline hydrolysis (✓) of **ester** (✓)

Examiner's comments:
*   This was generally well answered.

The student conducted further chemical tests on compounds **E** and **F** separately. The results of the tests are given in Table 4.2

Table 4.2

Expt	reagent	Result
3	PCl_5(s)	misty fumes were produced for both compounds **E** and **F**.
4	I$_2$, NaOH(aq), warm	pale yellow precipitate observed for both compounds **E** and **F**.

■■■   Based on experiments 3 and 4, what is the common functional group that could be present in both compounds **E** and **F**? Explain your answer, giving the type of reaction.

Both are **alcohols**. (✓)
They undergo **nucleophilic substitution** in Expt 3 and undergo **oxidation / positive iodoform test** in Expt 4. (✓)

OR   [1]

Both contain the following group, **RCH(OH)CH₃** or **-CH(OH)CH₃** (✓), and hence undergo **oxidation / positive iodoform test** (✓) with I_2, NaOH(a), warm.

Examiner's comments:

- This was generally not well answered.
- Common mistakes were stating wrong type of reactions e.g. "nucleophilic acyl substitution", "condensation" and giving wrong spelling e.g. "nucleophilic", "substituition".
- Some students concluded both E & F are alcohols based on Expt 3 alone and left out Expt 4 in their answer.

(iv) Using your answers in **(a)(i)** and **(a)(ii)**, draw the structure of compounds **E and F**.

Y   Z   [2]
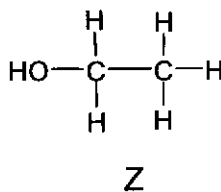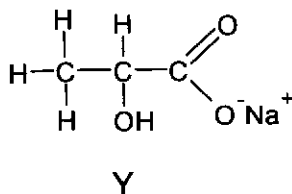
Examiner's comments:

- Most students are able to get the correct structure for compound F, but not E.
- Common mistakes for compound E were drawing a bond between O and Na, drawing a carboxylic acid, wrong position of the -OH group.

(v) The student now has enough information to determine the structural formula of **D**.
Draw the fully displayed structure of **D**.

                                                         [1]
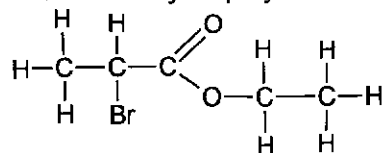
Examiner's comments:

- This proved difficult for many students. There is a significant number who left this part blank.
- Some students forgot about the alkyl bromide that is present in D (from a(i)). Students must learn to recognise that upon alkaline hydrolysis of ester D, the alkyl bromide present in the structure is also converted to alcohol (see Structure E).
- For those who could figure out the structure of D, some forgot to draw the displayed structure and hence got 0 mark.
- Some were not sure about the acid component and alcohol component of the ester and got them mixed up.

(b) Dichlorodiphenyltrichloroethane (DDT) is a well-known organochlorine pesticide that was widely used during the 20th century for controlling insect-borne diseases like malaria.

The equation below shows the environmental degradation of DDT to dichlorodiphenyldichloroethylene (DDE).

DDT   DDE
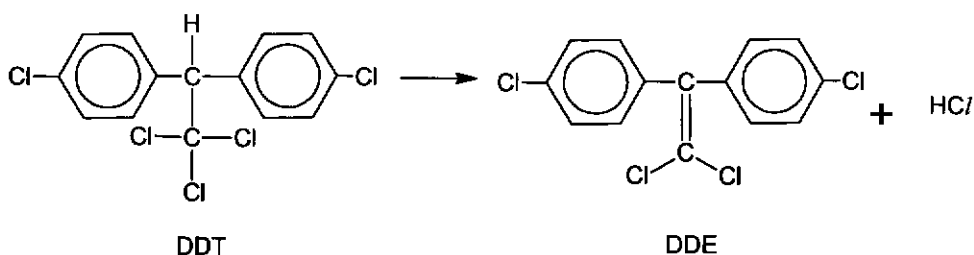
(i) State the type of reaction for the conversion of DDT to DDE.

elimination   [1]

Examiner's comments:

• This was generally well-answered.

Table **4.3** below shows the results when aqueous silver nitrate is heated with 0.5 mol of DDT and 0.5 mol of DDE separately.

	Time taken for ppt to appear	No. of moles of ppt formed per mole of compound reacted
DDT	5 min	x mol
DDE	no ppt	0 mol

Table **4.3**

(ii) What would be the value of x in Table 4.3?

1.5 mol   [1]

Examiner's comments:

• Only a small proportion of students answered this part correctly. Common mistake is "3 mol".
• Students should read the question carefully and note that 3 C-Cl bonds are present in DDT.
• Since 0.5 mol of DDT is used, hence 0.5 x 3 = 1.5 mol of AgCl ppt was formed.

(iii) Explain why no precipitate was observed for the reaction with DDE.

DDE contains 2 chlorobenzene (Cl bonded to benzene C) functional groups and two chloroalkene functional groups (Cl bonded to alkene C). All these 4 Cl groups are resistant towards nucleophilic substitution reactions.

Reason:

p-p orbital overlap (✓) between the chlorine and the 6 C atoms in benzene / 2 C atoms in C=C bond, results in the **delocalisation of lone pair of electrons on Cl** (✓) into the π-electron system of the **adjacent benzene** and **C=C bond** (✓), forming **partial double bond character** (✓*) in C-Cl. This strengthens the C-Cl bond, and hence does not undergo nucleophilic substitution.   [2]

(iv) In organic chemistry, a geminal compound is a molecule in which two or more identical or similar functional groups are attached to the same carbon atom.

When DDT reacts with hot aqueous NaOH, a gem-triol, is formed as an intermediate. A gem-triol contains three hydroxyl -OH groups bonded to the same carbon atom. The gem-triol formed is unstable and it readily converts to the final product, **S**.

S reacts with aqueous Na_2CO_3(aq) to liberate a colourless gas.

Draw the structure of the organic compound **S**.

[1]

S:
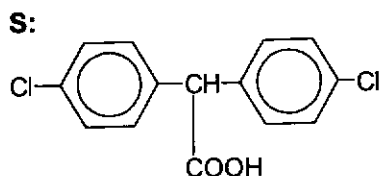
(c) (i) 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane, or o,p'-DDT, is an constitutional isomer of DDT.

The structure of o,p'-DDT is given below.
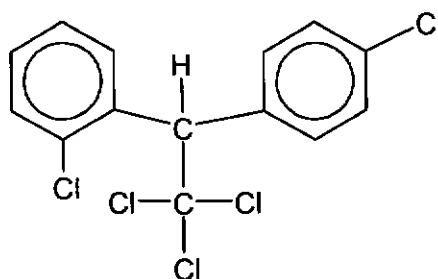
o,p'-DDT

State the type of stereoisomerism exhibited by o,p'-DDT.
Enantiomerism

(ii) Draw its isomers.

[2]

[Total: 14]

5 The pH of the seawater in the ocean is regulated by the carbonate - bicarbonate (CO_3^{2-} / HCO_3^-) buffer system.

Main buffering system: CO_3^{2-} + H_2O ⇌ HCO_3^- + OH^-

Recently, changes in the pH of the oceans by ocean acidification has been a concern. Ocean acidification is caused by the absorption of carbon dioxide (CO_2) from the atmosphere, and poses a significant threat to marine ecosystems worldwide.

The increased concentration of CO_2 in seawater leads to changes in the pH as shown by the graph below which shows the average ocean pH level worldwide from 1985 to 2020.
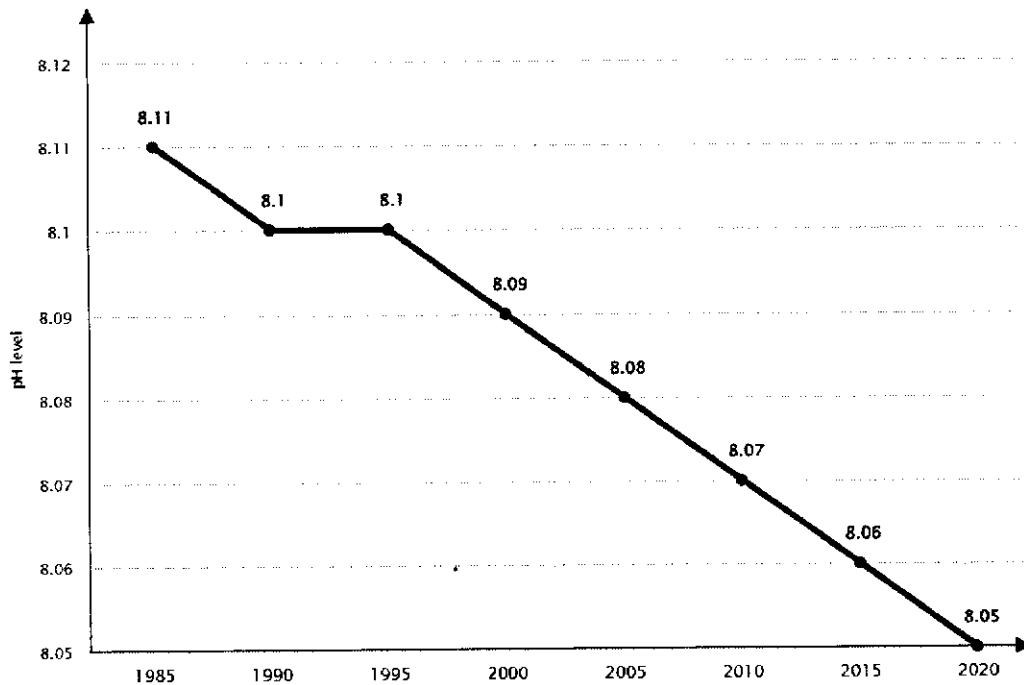
Fig. 5.1

(a) **(i)** Using the Fig 5.1, state and explain the trend of pH of the seawater of the ocean.

pH of seawater decreased. (✓)

CO_2 from the atmosphere dissolves in the seawater to produce H_2CO_3

which produces H^+ This increases the $[H^+]$ which cause the pH to   [1]

decease. (✓)

Examiner's comments:

This question was badly done as students merely state the trend but did not explain why the pH decreased. Just stating that there is an increased absorption of CO_2 do not warrant any credit as this was already written in the question. Some write about the equilibrium shift of $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ which fails to explain why H^+ is increasing.

(ii) With the aid of equations show how the carbonate - bicarbonate buffer system in seawater maintains the pH when there is an increase in amounts of H^+ or OH^- in the seawater.

upon addition of OH^-,
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

full arrow must be used

upon addition of H^+,
$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-$

[2]
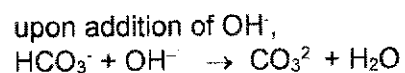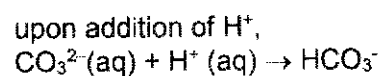
(iii) Use the pH value from Fig 5.1, show that the molar ratio of bicarbonate to carbonate ion of a sample of seawater from 2020 is 89:1.

Given that the K_b of CO_3^{2-} is 1.0×10^{-4} mol dm^{-3}.

Alkaline buffer:
$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
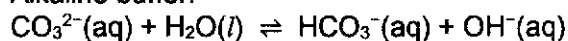
$$pOH = pK_b + lg\frac{[salt]}{[base]}$$

$$14 - 8.05 = -lg\,(1.0 \times 10^{-4}) + lg\frac{[HCO_3^-]}{[CO_3^{2-}]}$$

$$\frac{[HCO_3^-]}{[CO_3^{2-}]} = \frac{89}{1} \text{ (as shown)}$$

[2]

Examiner's comments:

(ii) This part was not well done as students only explained but did not write equations to show how the seawater maintains the pH. Some did not write the equation with irreversible arrow. So 1 mark was penalised overall if both equations are written with reversible arrow. Students must read the question carefully and answer it properly instead of writing in essay form when the qn only asked for equations.

(ii) This question proves to be difficult as may did not see this as an alkaline buffer. From Fi 5.1, they can get the pH of the seawater but need to change to pOH if using the formula for finding the ratio using buffer equation. If using pH value (8.05), the students must use the correct salt

and acid which is $8.05 = -lg\,(1.0 \times 10^{-10}) + lg\frac{[CO_3^{2-}]}{[HCO_3^-]}$.

The total CO_3^{2-} + HCO_3^- content of the seawater can be found by boiling a seawater sample with an excess of dilute sulfuric acid and absorbing the CO_2 evolved in a solution of barium hydroxide, $Ba(OH)_2$.

The precipitated barium carbonate, $BaCO_3$ can be filtered off, dried and weighed.

When a 100 cm³ seawater was treated in the above-mentioned process, 0.281 g of $BaCO_3$ was produced.

[Assume that the seawater sample is from the year 2020]

(iv) Show that the total amount of CO_3^{2-} + HCO_3^- content in the seawater sample is 1.42 x 10⁻³ mol.

After boiling with excess H_2SO_4, all HCO_3^- and CO_3^{2-} will be converted to CO_2.

CO_3^{2-} + H_2SO_4 → CO_2 + H_2O + SO_4^{2-}

$2HCO_3^-$ + H_2SO_4 → SO_4^{2-} + $2CO_2$ + $2H_2O$

(total) CO_2 + $Ba(OH)_2$ → $BaCO_3$ + H_2O
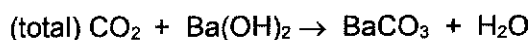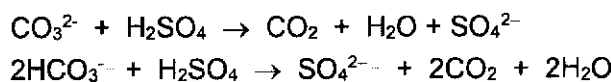
Amount of $BaCO_3$ formed = $\dfrac{0.281}{137.3 + 12.0 + 3(16.0)}$ = **1.42 x 10⁻³ mol**

Total amount of {CO_3^{2-} + HCO_3^-} in sample

= Total amount of CO_2 reacted with $Ba(OH)_2$

= Amount of $BaCO_3$ formed

= **1.42 x 10⁻³ mol** [1]

Examiner's comments:

Most just found the amount but may not know that (total) CO_2 + $Ba(OH)_2$ → $BaCO_3$ + H_2O. However, credit was given as long as working is shown how the amount was found.

(v) Hence, using the information in **(a)(iii)** & **(a)(iv)** calculate $[CO_3^{2-}]$ in the 100 cm³ seawater from 2020.

Let x be the original amount of CO_3^{2-} present in the seawater.

Since $\dfrac{[HCO_3^-]}{[CO_3^{2-}]}$ = 89, amount of HCO_3^- in seawater = 89x

Total amount of {CO_2 + HCO_3^-} = x + 89x = 90x = 1.424 × 10⁻³ mol

Amount of CO_3^{2-} in 100 cm³ seawater,

$x = \dfrac{1.424 \times 10^{-3}}{90}$ = 1.582 × 10⁻⁵ mol (ecf from iv answer)

$[CO_3^{2-}(aq)]$ in seawater = $1.582 \times 10^{-5} \times \dfrac{1000}{100}$ = 1.58 × 10⁻⁴ mol dm⁻³

[2]

(b) Organisms with calcium carbonate shells produce their shells according to the equation shown.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$
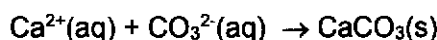
Changes in the pH alters the chemical balance of the oceans and affecting marine life, particularly organisms with calcium carbonate shells.

(i) Using the equations below and the concept of Le Chatelier's principle and solubility product, explain why marine organisms will not be able to build shells if pH of the seawater decreases.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s) \text{ -----(1)}$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \text{ -----(2)}$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s) \text{ ---(1)}$$
$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)\text{.......(2)}$$
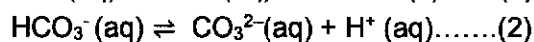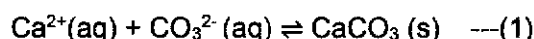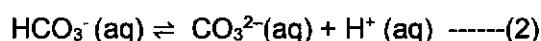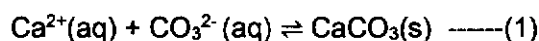
When pH decreases, [H⁺] increases, (✓) hence the following happens:
- By LCP, the position of equilibrium (2) shifts to the left (✓)to decrease [H⁺], hence [CO₃²⁻] decreases. (✓)
- **Eqm (1) shifts to left** (✓)to increase [CO_3^{2-} so $CaCO_3$ dissolves
- Ionic product of $CaCO_3$ drops to < K_{sp} ($CaCO_3$), (✓) hence
- precipitation of $CaCO_3$ is not possible. Therefore, marine organisms will not be able to build shells if pH of the seawater decreases.

[2]

(ii) The concentration of Ca^{2+} ions in the seawater sample from 2020 is 3.99×10^{-4} mol dm⁻³.

Given that K_{sp} $CaCO_3$ is 3.30×10^{-9} mol² dm⁻⁶, calculate the minimum [CO_3^{2-}] for the organisms to form their shells in 2020.

For precipitation, ionic product ≥ K_{sp}.

At first trace of precipitation, [Ca^{2+}] [CO_3^{2-}] ≥ 3.30×10^{-9}

$$(3.99 \times 10^{-4}) [CO_3^{2-}] \geq 3.30 \times 10^{-9}$$

$$[CO_3^{2-}] \geq \underline{8.27 \times 10^{-6} \text{ mol dm}^{-3}}$$

[1]

(iii) Using your answer in **(a)(v)** and **(b)(ii)**, explain whether the organisms will be able to form their shells in the seawater in 2020?

It will form the shell as $[CO_3^{2-}]$ in the seawater > the minimum $[CO_3^{2-}]$ = 8.27×10^{-6} mol dm^{-3}

$[IP > K_{sp}]$. [1]

[allow ecf as long as concept is correct]

Examiner's comments:

This was well done but some found IP of $CaCO_3$ when the qn specifically stated that to use answer in (a)(v) and (b)(ii) so just need to compare the concentration of $CaCO_3$ in seawater and the minimum concentration of $CaCO_3$ needed for precipitation.

[Total: 12]

6 **(a)** Haemoglobin and hemocyanin are two oxygen-transporting proteins found in living organisms. Both proteins are coloured due to the presence of transition metals, such as iron in haemoglobin and copper in hemocyanin, that form complexes essential for their oxygen-binding properties.

(i) Why are transition metal complexes coloured?

In complexes, lone pairs on the approaching ligands cause a <u>splitting of</u> [3] <u>the energy of d-orbitals into 2 groups</u> with an energy gap, ΔE, between them.

When a <u>d-electron from lower energy group is promoted to the higher</u> <u>energy group</u> (d-d transition), <u>wavelengths of visible light that</u> <u>corresponding to ΔE is absorbed</u>.

<u>Colour of the complex will be complementary to the wavelengths of the</u> <u>light absorbed</u>.

<u>Examiner's comments</u>:

Students who use their own words to write answers usually missed out the key points. Some explanation was vague and hence credit was not given. It is advisable for students to memorise the key points.

(ii) Non-transition metal compounds, in contrast, tend to be colourless. Explain why a solution containing $[Mg(H_2O)_6]^{2+}$ is colourless.

Mg^{2+}: $1s^2 2s^2 2p^6$

Since Mg^{2+} has <u>no d electron</u> (✓), hence <u>d–d transition is not possible</u> (✓), visible light is not absorbed thus $[Mg(H_2O)_6]^{2+}$ is colourless.

OR [2]

The <u>energy gap from highest occupied orbitals to the next empty orbital</u> <u>is too large</u> (✓), which requires <u>absorption of radiation outside of visible</u> <u>region.</u> (✓)

Examiners' comments:

What examiners are looking out for

1) no d electron
2) hence, **no d to d electronic transition** thus no visible light is absorbed
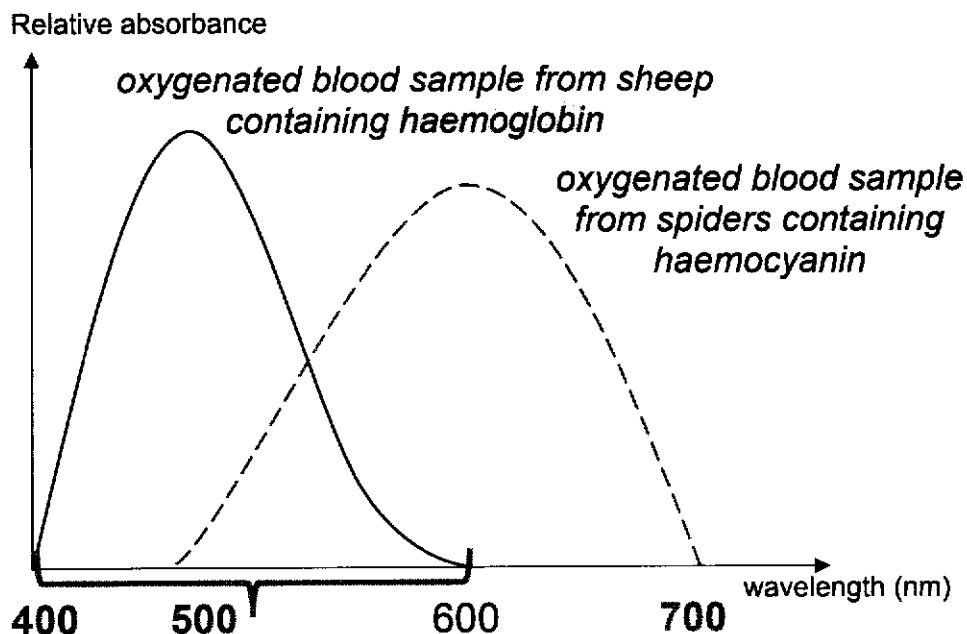
Misconceptions including below:

- Some said Mg^{2+} has fully filled d subshell which is wrong it has empty d subshell
- Some wrote about ligand exchange that has nothing to do with this

Absorption spectra, an analytical method in chemistry, show the wavelengths of light absorbed by substances.

Chemists use this technique to analyse the oxygenated blood samples from sheep (haemoglobin) and spiders (haemocyanin) to compare their absorption characteristics.
The result of the analysis is shown in Fig. 6.1.

Relative absorbance

oxygenated blood sample from sheep containing haemoglobin

oxygenated blood sample from spiders containing haemocyanin

wavelength (nm)

400   500   600   700

Haemoglobin absorb shorter wavelength
=> absorb higher frequency =>higher ΔE

The wavelengths associated with each colour of visible light are given below. Light of a longer wavelength is lower in energy than light of a shorter wavelength.

colour of visible light	wavelength (nm)
red	620 – 750
orange	590 – 620
yellow	570 – 590
green	495 – 570
blue	450 – 495
violet	380 – 450

(iii)   The oxygenated blood of sheep, which contains haemoglobin, is red. Using this information and the data provided, predict the colour of the oxygenated blood of spiders, which contains haemocyanin.

Blue / Violet

[accept blue-violet]

Examiner's comments

Analyse the absorbance curve given: qn states blood of sheep, which contains haemoglobin, is red.

Look carefully at the graph, haemoglobin DID not absorb red light energy – thus it appears red.

(Because the colour observed/ something appears as is COMPLEMENTARY to what is absorbed!)

Look at graph, haemocyanin did not absorb 400-500nm which is violet or blue thus it appears violet/ blue.

(iv) What deduction can be made from the absorption spectra in Fig. 6.1, about the size of the d-orbital splitting in the two samples of oxygenated blood, containing different complexes of haemoglobin & haemocyanin? Explain your answer.
The d-orbital splitting/energy gap in the complex of <u>haemoglobin is larger</u> than haemocyanin.

This is because <u>**shorter wavelength of light**</u> (**higher frequency of light**) is absorbed, indicating that ΔE is larger ie. electron in lower d-orbitals absorbs <u>**more energy**</u> to be promoted to the higher d-orbitals. [2]

$$\Delta E = hf = \frac{hc}{\lambda}$$

where **h is Planck's constant**
c is the speed of light
λ **is the wavelength of radiation absorbed**
f is the frequency of radiation absorbed
c = fλ (c = constant, when f↑, λ↓)

Hence $\quad \dfrac{c}{\lambda} = f$

[Total:7]

(b) The van Arkel triangle, invented by Dutch chemist Anton Eduard van Arkel, is a tool used to classify the bonding in compounds as ionic, covalent, or metallic.

Fig. 6.2 shows an example of a van Arkel triangle.

The **y-axis represents the difference in electronegativity between two elements**, while the **x-axis shows the average electronegativity**.
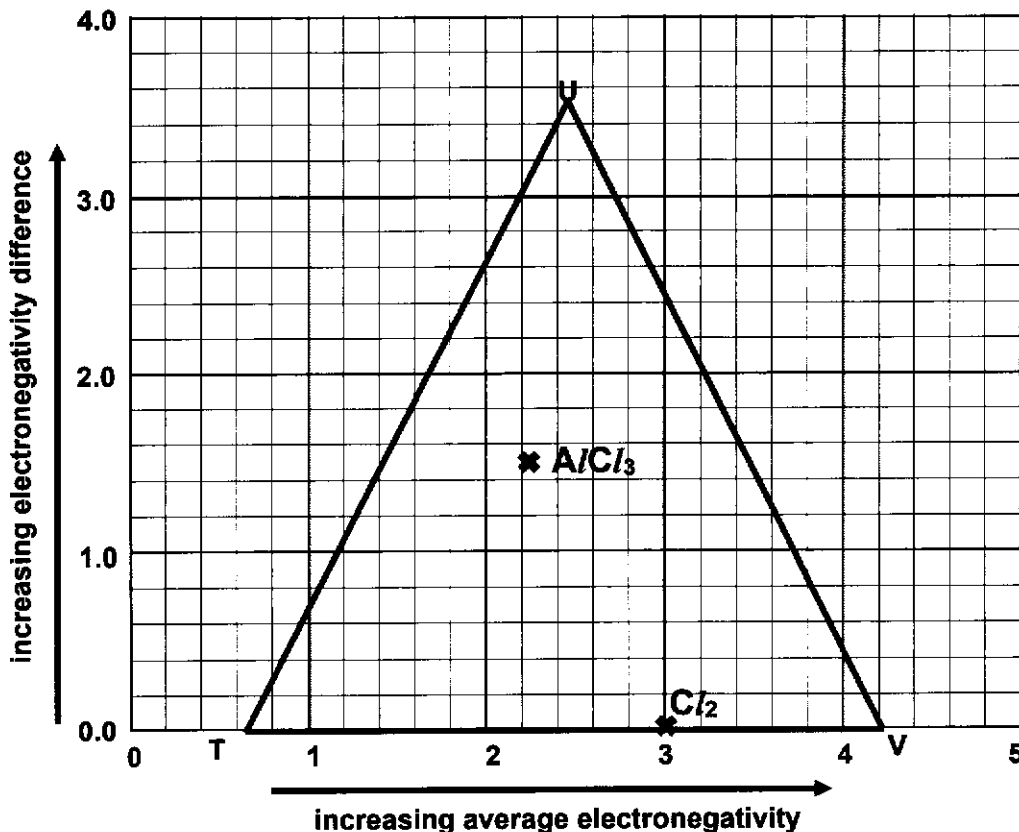

Fig. 6.2

Table 6.1 provides the electronegativity values of some of elements from Period 3 of the Periodic Table, based on Pauling's Scale. The average electronegativity is calculated based on the sum of the electronegativities of the two elements in the compound, divided by two.

Table 6.1

Element	Electronegativity
Na	0.9
Mg	1.2
A*l*	1.5
Si	1.8
P	2.1
S	2.5
C*l*	3.0

(i) Plot the position of C*l*$_2$ and A*l*C*l*$_3$ on the diagram. Label your points clearly in Fig. 6.2. [2]

(ii) The three extremes on the van Arkel triangle, namely **T**, **U** and **V**, represent the three types of chemical bonding, metallic, ionic and covalent.

State the correct type of bonding present at each of the bonding extremes.

Pls know definition of electronegativity: **Electronegativity** is a measure of the tendency of an atom to attract a bonding pair of electrons.

T: metallic
(metals are low in electronegativity, don't want to attract electrons to itself, want to lose electrons)
U: ionic (big difference in electronegavity => tends to be ionic)
V: covalent (higher in electronegativity. Cl-Cl bond has zero difference in electronegativity as both Cl has same electronegavity)   [2]

Examiner: Quite well done, most get at least 1 or 2 marks.

(c) **(i)** In the liquid state, $AlCl_3$ exists as a compound with a molar mass of 267 g mol^{-1}.
Draw the structure of this compound.
Molar mass of 267 g mol^{-1} is twice mass of $AlCl_3$, showing 2 molecules of $AlCl_3$ dimerised.

[1]
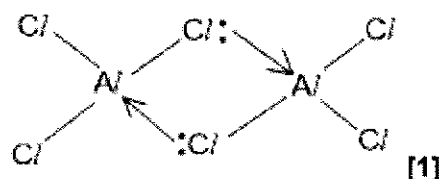
Examiner: **Pls show lone pair and dative bonds**

(ii) The boiling points of Al_2O_3 and $AlCl_3$ in the liquid state are 2977 °C and 180 °C respectively.

Explain, in terms of structure and bonding, the difference in their boiling points.

Al_2O_3 has a giant ionic lattice (✓) structure while $AlCl_3/Al_2Cl_6$ has a simple molecular (✓) structure.

More energy is required to overcome the stronger ionic bonds / electrostatic forces of attractions between Al^{3+} and O^{2-} ions (✓) than the weaker id-id interactions between $AlCl_3/Al_2Cl_6$ molecules (✓).   [2]

Examiner: Huge misconceptions:
A significant number wrongly think Al_2O_3 is giant covalent or simple covalent structure.

Note Al is metal, O is non metal. Metal and non-metal combine to form IONIC compounds – O level knowledge, with exception of $AlCl_3$ which is simple covalent – that you can infer from low boiling point of 180 °C!

Common mistakes: Miss out structures: giant ionic lattice structure or $AlCl_3/Al_2Cl_6$ has a simple molecular or **simple covalent** structure.

Some thought $AlCl_3$ **is polar with pd-pd attraction between molecules – this is wrong because** $AlCl_3$ is non-polar no net dipole moment
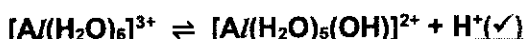
(iii) The pH values of the solutions of two Period 3 chlorides are given below.

compound	pH of 1.0 mol dm^{-3} solution
MgCl$_2$	**X**
AlCl$_3$	**Y**

[3]

Write equations for the reaction of AlCl$_3$ with water.

State the values of x and y in the table above. Briefly explain the different pH values of the two chloride solutions.

AlCl$_3$ + 6 H$_2$O → [Al(H$_2$O)$_6$]$^{3+}$ + 3Cl$^-$ (✓)

[Al(H$_2$O)$_6$]$^{3+}$ ⇌ [Al(H$_2$O)$_5$(OH)]$^{2+}$ + H$^+$(✓)

x = 6.5 (✓)

y = 3(✓)

Since Al^{3+} has higher charge density(✓) **than Mg^{2+}, it has a greater degree/ extent of hydrolysis**(✓) **in aq solution, resulting in lower pH.**

Examiner comments: Most common confusion was mixing up period 3 chlorides with oxides pls revise! Key concept for Period chlorides = hydrolysis
Key concept for oxides = acid base behaviour of oxides

Charge density is for ION eg. Al^{3+} not for AlCl$_3$

(iv) The lattice energy of magnesium chloride is −2582 kJ mol^{-1}. Some enthalpy changes of hydration are listed in Table 6.4.

Table 6.4

Ions	ΔH_{hyd} / kJ mol^{-1}
Mg^{2+}	−1980
Cl$^-$	−381

Using the data provided, calculate the enthalpy change of solution of magnesium chloride.

ΔH_{soln}(MgCl$_2$) = − LE + $\Sigma\Delta H_{hyd}$(ions)
= − (−2582) + (−1980) + 2(−381)
= **−160.0 kJ mol^{-1}** (3sf + sign + units) [1]

[1]

Examiner comments: Forgot the equation

ΔH_{soln}(ionic compound) = − LE + $\Sigma\Delta H_{hyd}$(ions)

and forgot to substitute coefficient of Cl$^-$ ie. 2

[Total:18]